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54 **Extrusion finishing of perfluorinated copolymers.**

57 Unstable backbone links in melt-processible tetrafluoroethylene copolymers can be reduced by subjecting the copolymer to high shear under specified pressure and temperature conditions in a chamber such as a twin-screw extruder.

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TITLE

EXTRUSION FINISHING OF PERFLUORINATED COPOLYMERS

FIELD OF THE INVENTION

This invention relates to treatment of raw
5 perfluorinated copolymers to improve their thermal
stability.

BACKGROUND

The aqueous dispersion copolymerization of
tetrafluoroethylene (TFE) with perfluorinated alpha
10 olefins such as hexafluoropropene (HFP) produces a
raw product which must be further treated or
"finished" before being melt fabricated into a useful
final product. A major purpose of the "finishing" is
to remove all sources of volatiles which could cause
15 bubbles or voids in the final product.

Several sources of volatiles can exist in
the unfinished or raw polymers including unstable
endgroups and unstable backbone linkages. Various
types of endgroups are possible but use of the common
20 persulfate initiator leads to carboxylic acid
endgroups. The degradation of these carboxylic acid
ends can be a major source of volatiles at
fabrication temperatures as was discussed in U.S.
Patent 3,085,083 (R. C. Schreyer). The polymer
25 endgroups after extrusion may also be vinyl
($-\text{CF}=\text{CF}_2$), difluorohydride ($-\text{CF}_2\text{H}$), internal
olefin [$-\text{CF}=\text{CF}(\text{CF}_2)\text{CF}_3$, $(\text{CF}_2)_n\text{CH}_3$, or
carboxylic acid fluoride ($-\text{COF}$). The relative
amounts of these ends will be dependent on the
30 extrusion conditions, the type of initiator, the
presence of salts which can catalyze the
decarboxylation, and moisture level.

The second source of volatiles is believed
to be due to the presence in the polymer backbone of
35 relatively unstable linkages which thermally degrade

during fabrication. These links may be present even if the polymer has stable endgroups directly from polymerization. The elimination of most of these links is desirable to achieve a low volatiles level.

5 The structure(s) of the unstable backbone linkages in perfluorocopolymers have not been indentified but appear to be comonomer diads not involving TFE. Thus in TFE/HFP copolymers the unstable backbone linkage arises from two adjacent HFP units. The volatiles

10 arising from initial thermal degradation of TFE/HFP copolymer flake (unfinished) are very rich in HFP monomer. The level of unstable backbone linkages in HFP/TFE copolymers appears to be an inverse function of molecular weight (and melt viscosity). This

15 suggests that the HFP diad forms by combination as the termination mechanism in polymerization. Regardless of the structure of the polymer backbone instability, a concentration can exist which causes problems with bubble formation during melt

20 fabrication.

SUMMARY OF THE INVENTION

It has been found that unstable backbone links may be removed under conditions of high shear such as in a twin screw extruder which is designed to

25 achieve good mixing and high shear.

Specifically, the process of this invention is a process for preparing a thermally stable copolymer which comprises

a) subjecting in a chamber a raw (i.e., as

30 polymerized) melt-processible copolymer of 80-99% by weight units of tetrafluoroethylene and complementally 20-1% by weight units of at least one ethylenically unsaturated copolymerizable comonomer, which copolymer has a backbone volatiles index

35 greater than 15 and a melt viscosity between 10^2 and 10^6 Pa·s, to an absolute pressure of less than

10⁵ Pa and at a temperature of between 220°C and 450°C while moving the copolymer through the chamber and subjecting the copolymer to a shear rate between 500 and 7000 reciprocal seconds for a time sufficient
5 to result in the copolymer having a backbone volatiles index less than 15; and

b) removing the copolymer from the chamber. Preferably, the chamber will be an extruder, and most preferably a twin screw extruder that
10 contains kneading blocks.

Preferably, an absolute pressure of less than 10⁴ Pa will be employed.

Preferably, the copolymerizable comonomer will be hexafluoropropylene.

15 Preferably in step b), and particularly if subsequent finishing steps are to be carried out such as filtering or fluorinating, it is most convenient to remove the polymer from the chamber by attaching an extruder or another melt pumping device to the
20 chamber and removing the copolymer simply by extruding it through this added extruder or pumping device, which may be a single screw extruder.

DESCRIPTION OF THE INVENTION

TFE copolymers are melt-processible
25 fluorine-containing resins for instance, TFE/alpha olefins such as TFE-hexafluoropropylene copolymer. These melt-processable fluorine-containing resins are melt-flowable, that is, the melt viscosity of these resins is generally lower than 10⁶ poises at an
30 optimum processing temperature and, therefore, they provide a film having less pinholes and voids as compared with polytetrafluoroethylene which has an excellent chemical and corrosion resistance but has no melt-flowability or melt-processability since it
35 has an extremely high melt viscosity of from 10¹⁰

to 10^{11} poises even at a processing temperature of about 380°C .

If the chamber employed is an extruder, the approximate shear rate can be calculated by the following formula:

$$\dot{\epsilon} = \frac{\pi DN}{h}$$

α = shear rate, s^{-1}
 D = diameter of the screw (millimeters)
 N = revolutions per second
 h = the distance between the screw
 and the barrel wall (in millimeters)
 $\pi = 3.1416$

Shear rates will be highest at the screw tips and kneading block crests.

The temperature range employed is from 220 to 450°C with the preferred range from 240 to 400°C .

The residence time employed is that needed to reduce the backbone volatiles index to the values recited above. Generally this will be between about 1 and 30 minutes.

If the polymer removed from the chamber contains unstable endgroups or if it has poor color, these problems can be eliminated by fluorination. The fluorination may be carried out with a variety of fluorine radical generating compounds under a variety of conditions as described in British Patent 1210794. Preferably the polymer is contacted with a fluorine/inert gas mixture at an elevated temperature which is below the melting point of the polymer. If the fluorination is carried out in a partially filled (with polymer) container through which a fluorine/inert gas mixture is passed with agitation of the polymer to continually expose new surfaces, then the temperature may be 100°C - 250°C with a preferred temperature of 130°C - 200°C and the residence time may be 30 minutes to 12 hours, with a

longer time being required with lower temperatures. A 25/75% mixture of fluorine/nitrogen is preferred as the fluorinating medium. The unstable ends are convert by the action of fluorine to perfluoromethyl
5 (-CF₃) ends with the exception of carboxylic acid fluoride ends (which react very slowly with fluorine). Quantitative measurements of the endgroups may be made by infrared analysis as described in U.S. Patent No. 3085 083.

10 If the resin to be processed contains -CF=CF₂ end groups or end groups which are convertible to -CF=CF₂ end groups, then acid fluoride (-COF) ends may form by oxidation of the -CF=CF₂ groups. Acid fluoride ends are resistant
15 to stabilization techniques such as fluorination and thus should be minimized during the extrusion process. This may be done in two ways 1) The flake and the flake handling equipment may be sparged with nitrogen to remove atmospheric oxygen which might
20 otherwise oxidize the vinyl end groups, (time of contact with nitrogen will be a time sufficient to essentially remove all absorbed and adsorped oxygen), and 2) water may be injected into the extruder with the polymer so that any acid fluoride ends which are
25 formed may be hydrolyzed to carboxylic acid ends. The required level of moisture addition depends on the level of acid fluoride ends which in turn depends on the type of end groups in the polymer feed and the severity of the extrusion conditions, but generally
30 will be between 0.5-1.5% by weight based on copolymer.

The application of vacuum to the process functions to remove gases from resin degradation, excess water (if used), and low molecular weight fluoro-oligomers.

It should be apparent that techniques other than fluorination may also be utilized to eliminate unstable endgroups. One such method is humid heat treatment disclosed in US patent 3085083.

5 Certain initiators such as the perfluoroacyl peroxides $[F(CF_2)_nCO_2]_2O$ give predominantly stable endgroups directly from polymerization and therefore do not require fluorination.

Test Procedures

10 Standard melt viscosities of the polymers were measured according to American Society for Testing and Materials test D-1238-52T, modified as follows: The cylinder, orifice and piston tip are made of a corrosion-resistant alloy, Haynes Stellite
15 19, made by Haynes Stellite Co. The 5.0g sample is charged to the 9.53mm (0.375 inch) inside diameter cylinder, which is maintained at $372^\circ C \pm 1^\circ C$. Five minutes after the sample is charged to the cylinder, it is extruded through a 2.10mm (0.0825 inch)
20 diameter, 8.00mm (0.315 inch) long square edge orifice under a load (piston plus weight) of 5000 grams. This corresponds to a shear stress of 44.8 KPa (6.5 pounds per square inch). The melt viscosity in Pa's is calculated as 5317 divided by the observed
25 extrusion rate in grams per minute.

The tendency of fluoropolymer to give bubbles during fabrication has been previously measured by a "volatiles index" test. This test measures the pressure built up by heating a polymer
30 sample to $380^\circ C$. This pressure rise is the result of desorbed dissolved gases and polymer endgroup and backbone degradation. The primary purpose of the invention described herein is the removal of unstable backbone linkages. Thus all of the examples shown
35 herein were treated with fluorine to remove unstable

endgroups before analysis of volatiles content. A modification of the "volatiles index" test is employed to remove the contribution of dissolved gases, especially air, in the polymer to the observed pressure rise. In the procedure which was employed here, a 10.0g (w) sample of the resin is placed in an aluminum foil thimble which is charged into a glass tube equipped on its top with a manometer. The tube is evacuated to 0.1-2mm Hg (13.3 - 267 Pa) and then upon reaching equilibrium, is placed in a hot block maintained at 150°C for three hours. The tube is reevacuated to remove the desorbed gases and then the tube is placed in a hot block maintained at 380°C for at least 40 minutes. The pressure readings are recorded as a function of time. The backbone volatiles index is calculated by the following equation:

$$\text{Backbone V.I.} = \frac{(P_{40} - P_0) V}{10 w}$$

wherein P_{10} and P_{40} are the pressures of the sample in mm Hg after 10 and 40 minutes in the hot block, V is the volume of the tube in ml, and w the sample weight in grams. The volume of the apparatus was 110±10ml.

When the analysis is performed as described above, a high "backbone volatiles index" indicates a relatively high level of polymer chain backbone unstable linkages which can potentially degrade and give volatiles and bubbles during melt fabrication of the resin such as into a molded article or as a coating onto wire. The "backbone volatiles index" should be less than 15, preferably less than 10, to avoid an amount of bubbles formed upon fabrication which is detrimental to the resin properties.

Color of the extruded or the extruded and fluorinated cubes was determined by projecting white light onto a sample, and passing the reflected light through filters and measuring it with a photocell. A high percent green (%G) reflectance indicates a high level of whiteness of the cubes. The colorimeter used in the examples was a "DuColor" colorimeter.

The color of the cubes as-extruded is dependent upon the severity of the extrusion conditions, the level and type of polymerization initiator residues present, and the level of contamination, if any. The color after subjecting to shear can be quite dark. Fluorination results in essentially white cubes as shown by the high %G values.

EXAMPLES

Reduction of Backbone Volatiles by Shear

Several tetrafluoroethylene/hexafluoropropylene copolymer (TFE/HFP copolymer) flake samples which had been polymerized with ammonium persulfate (APS) or mixed ammonium/potassium persulfate (APS/KPS) initiators and which had various melt viscosities as-polymerized, were finished as described below to give products having a reduced tendency to form bubbles upon melt-fabrication.

The experiments were carried out with a twin screw extruder, equipped with a vacuum port and vacuum system, which fed into a single screw extruder which was also equipped with a vacuum port and a screen pack and die. The twin screw extruder served as a resin melter and a reactor in which the desired backbone stabilization was conducted. The single screw extruder was used as a melt pump to generate the pressure necessary to move the resin through the screen pack and then the die. Vacuum was applied to remove volatiles from the molten resin.

The extrusion equipment described above is a "Kombiplast" extruder from the Werner and Pfleiderer Corporation. Corrosion-resistant materials were used for those parts which came into contact with the polymer melt. The twin-screw extruder had two corotating screws disposed side by side. The screw configurations were designed with an intermeshing profile and tight clearances, causing them to be self-wiping. The screw configurations included kneading blocks and conveying sections but the highest shear occurs in the kneading block sections. The screws contained three matched kneading block sections. In addition to the tight clearance in the kneading blocks, high screw speeds (up to 162 rpm) contributed to the high shear.

The twin screw extruder emptied into a single screw melt pump which was designed to generate pressure at low shear rates for filtration through the screenpack. The single screw extruder had a vacuum port at its rear where the melt arrived from the twin screw extruder. The screenpack contained several different screen sizes, the smallest being 200x600 mesh.

The die contained either 15 or 28 (larger number of die holes was used with higher viscosity resin) 2.5mm diameter holes and the extruding melt was melt-cut into pellets which were cooled by a stream of water. The pellets were cylindrically shaped about 3.5mm in diameter and 1.5-3.0mm thick.

The details of the extrusion conditions are shown in Table I.

TABLE I

EXTRUSION DATA - EXAMPLES 1, 2 AND 3

	<u>Parameter</u>	<u>Example</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
5	Polymerization Initiator	APS/KPS	APS	APS/KPS
	Feed MV (kPa's)	11.2	25.0	148.
	<u>Twin Screw Conditions</u>			
	Rate (g/s)	17.7	17.3	13.2
10	Shear Rate, s ⁻¹ Channel	63	83	46
	kneading Block Crest	1380	1770	980
	Screw Speed (rpm)	124	162	90
	Barrel Temp. °C	360	370	310
	Power (kW)	3.3	8.5	6.0
	Hold Up Time, s	576	324	792
	Vacuum Port Pressure (kPa)	5.8	6.5	7.5
15	Melt Temperature (exit), °C	316	352	323
	<u>Single Screw Conditions</u>			
	Shear Rate, s ⁻¹ Channel	2.0	3.5	9.2
	Clearance	97	170	450
	Screw Speed (rpm)	8	14	37
	Barrel Temp. °C	360	370	350
20	Power (kW)	2.0	3.8	9.4
	Hold Up Time, s	300	300	402
	Vacuum Port Pressure (kPa)	12.3	11.6	13.3
	<u>Screen Pack Conditions</u>			
	Pressure (MPa)	10.1	15.2	21.4
25	Hold Up Time, s	800	820	1075
	<u>Die Conditions</u>			
	Number of Die Holes	15	15	28
	Pressure (MPa)	6.7	8.3	9.3
	Melt Temperature (°C)	365	372	365
30	<u>Product Properties</u>			
	Melt Viscosity (kPa's)	9.5	22.5	68.3
	%G	5	18	5

35 The extruded pellets had the melt viscosities shown in Table I. The pellets were gray-brown in color as indicated by the low % G

values (also in Table I). Endgroup analyses indicated that the pellets still contained some unstable endgroups, especially the sample of Example 2. The pellets were then exposed to fluorine gas to improve the color and eliminate the remaining unstable endgroups.

Subsequent Fluorination

A fluorination reactor was used, which was a modified double cone blender equipped with gas inlet and vent connections and an electric heating mantle. The gas inlet dipped down into the tumbling particles and the vent pointed up into the vapor space and both are held stationary within the rotating blender. The polymer pellets were placed in the reactor which was then sealed and rotation was begun at 5 rpm. The polymer pellets were heated with the electric mantle on the reactor and also with hot filtered air. When the polymer reached the desired temperature, the air stream was cut off and a vacuum was applied to the reactor to remove all air. A mixture of fluorine/nitrogen (25/75 volume %) was fed through the reactor for the desired time period while maintaining the temperature with the electric mantle heater. The conditions of fluorination are summarized in Table II.

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TABLE II

<u>Example</u> <u>Sample</u>	<u>Polymer</u> <u>Charge</u> ¹	<u>Fluorination Time</u>	<u>Fluorination Temperature</u>	<u>Fluorine Added</u> gm/Kg polymer
1	44%	5 hours	190°C	2.49
2	60%	4 hours	190°C	1.65
3	58%	4 hours	190°C	0.82

(1) Volume % of fluorinator capacity.

At the end of the fluorination cycle, the fluorine and the electric mantle heats were turned off and the reactor was once again evacuated slowly. The residual fluorine was then purged from the reactor with nitrogen. The nitrogen purge was checked for fluorine with moist potassium iodide paper (paper will darken in presence of fluorine). When the fluorine was gone, the gas flow was switched to cold air for cooling. After the batch was cooled, it was dropped.

The endgroup analyses showed almost complete removal of all unstable end groups. (See Table III) Other analyses of the fluorinated pellets are shown in Table IV. The color of the pellets was clear white and this is indicated by the high % G values.

The "backbone volatiles index" (BVI) values of the extruded and fluorinated pellets shown in Table IV are all well below the minimum of 15 which is believed to be necessary to permit bubble-free fabrication. The "backbone volatiles index" of the flake (fluorinated to remove endgroups) from which the examples were extruded are also shown in Table IV and are all greater than 15. It is apparent that the shear generated during extrusion is necessary to achieve a low "backbone volatiles index."

TABLE III
ENDGROUP ANALYSES

	Example Sample	Endgroup*	Endgroups per 10^6 C Atoms	
			Before Fluorination	After Fluorination
5	1	-COF	0	0
		-CO ₂ H(m)	2	5
		-CF=CF ₂	51	16
		-CO ₂ H(D)	0	0
10	2	-COF	24	2
		-CO ₂ H(m)	51	7
		-CF=CF ₂	226	12
		-CO ₂ H(D)	19	0
15	3	-COF	0	0
		-CO ₂ H(m)	0	2
		-CF=CF ₂	21	4
		-CO ₂ H(D)	0	0

Note: N.A. - not analyzed. *Two types of -CO₂H endgroups are seen by infrared, the monomeric -CO₂H(m) ends and the dimeric or hydrogen bonded CO₂H(D) ends.

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Extruded, Sheared and Fluorinated Pellets

Example Sample	Fluorinated Flake		(Not subjected to shear)		Extruded and Sheared pellets (But not Fluori- nated)		Extruded, Sheared and Fluorinated Pellets	
	MV	BVI	MV	%G	MV	%G	BVI	%G
1	9.10	20	9.5	5	8.67	51	7.6	51
2	13.7	17	22.5	18	14.3	54	5.7	54
3	88	16	68.3	5	45.0	49	3.4	49

Control of Acid Fluoride Endgroups

An experiment was carried out to show the effect of water addition to a twin screw extruder similar to the one used in the first section of these
5 Examples on the level of acid fluoride endgroups in the extruded product. The feed was a HFP/TFE copolymer which had been polymerized with mixed APS/KPS initiator and had a melt viscosity of 37.3 kPa's and an HFP content of 10.0 weight percent. The
10 extrusion equipment was similar to that described above except on a smaller scale. A 28mm twin-screw extruder fed the polymer into a 38mm single screw extruder and then through a screen pack and die. The resin was extruded with and without water addition
15 (1.0% directly to the twin screw feed throat) under otherwise identical conditions. The resin extruded without water addition contained 37 acid fluoride ends per 10^6 carbon atoms whereas the resin extruded with water addition contained no detectable
20 acid fluoride ends.

Another experiment was carried out to show the effect of nitrogen sparging on acid fluoride end group formation. The same polymer feed and the same equipment were used as was described above for the
25 experiments with water addition. It was found that sparging of the flake in the extruder feed bin to remove essentially all absorbed and adsorbed oxygen was not effective in reducing acid fluoride ends. However, when the flake was sparged with nitrogen
30 under reduced pressure overnight and then fed to the extruder through a nitrogen blanketed feed system, no acid fluoride end groups were found in the extruded product. Apparently, the fluoropolymer flake contained enough absorbed and adsorbed air (oxygen)
35 that a prolonged sparging was required. A control

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(no nitrogen sparging or water addition) for this experiment contained 22 acid fluoride end groups per 10^6 carbon atoms.

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CLAIMS

1. A process for preparing a thermally stable copolymer which comprises
 - a) subjecting in a chamber a raw melt-processible copolymer of 80-99% by weight units of tetrafluoroethylene and complementally 20-1% by weight units of at least one ethylenically unsaturated copolymerizable comonomer, which copolymer has a backbone volatiles index greater than 15 and a melt viscosity between 10^2 and 10^6 Pa.s, to an absolute pressure of less than 10^5 Pa at a temperature of between 220°C and 450°C while moving the copolymer through the chamber and subjecting the copolymer to a shear rate between 500 and 7000 reciprocal seconds for a time sufficient to reduce the backbone volatiles index of the copolymer to less than 15; and
 - b) removing the copolymer from the chamber.
2. A process according to claim 1 wherein the chamber is a twin screw extruder that contains kneading blocks.
3. A process according to claim 1 or 2 wherein the copolymer is a copolymer of tetrafluoroethylene and hexafluoropropylene.
4. A process according to claim 1, 2 or 3 wherein after step b), the copolymer is contacted with fluorine gas while agitating the copolymer.
5. A process according to any one of the preceding claims wherein water is added to the chamber in an amount sufficient to remove all acid fluoride end groups.
6. A process according to any one of the preceding claims wherein the copolymer is contacted with nitrogen to remove essentially all absorbed and adsorped oxygen from the copolymer immediately prior to carrying out step a).
7. Shaped articles melt fabricated from a thermally stable copolymer prepared by a process as claimed in any one of the preceding claims.

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EUROPEAN PATENT APPLICATION

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⑤④ **Extrusion finishing of perfluorinated copolymers.**

⑤⑦ Unstable backbone links in melt-processible tetra-
fluoroethylene copolymers can be reduced by subjecting
the copolymer to high shear under specified pressure and
temperature conditions in a chamber such as a twin-screw
extruder.



European Patent
Office

EUROPEAN SEARCH REPORT

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EP 85 30 0266

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D, A	US-A-3 085 083 (R. COURTENAY SCHREYER) * Claims 1-6 *	1	C 08 F 8/50
A	US-A-2 933 536 (L.A. WALL) * Claims 1-3 *	1	
A	GB-A-1 496 347 (AKADEMIE DER WISSENSCHAFTEN DER DDR) * Claims 1-9; example 1 *	1	
A	US-A-3 862 265 (R.A. STEINKAMP) * Claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17-06-1986	Examiner PERMENTIER W.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

